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Effect of the P3HT:ThCBM growth rate on solar cell performance

We present a study of the morphology and electrical properties of photovoltaic devices consisting of blends of regioregular poly(3-hexylthiophene) (P3HT) as electron donor and [6,6]-thienylC_{61} butyric acid methyl ester($[60]$ThCBM) as an electron acceptor. The solar cells were fabricated by depositing the photoactive layer from solvents with different boiling points. In this way we control the growth rate of the films. Atomic force microscopy analysis reveals a more granular structure in case of fast grown films, as well as a well-defined fibrilar and crystalline structure for slowly grown films. Electrical characterization of the solar cell devices indicates a clear advantage of the slow growth procedure. This results in an order of magnitude enhancement in the hole mobility through the P3HT phase. As a consequence of a more balanced transport of electrons and holes in the blend and an 0.4% (absolute) increase in power conversion efficiency. Additionally, it is shown experimentally that optimum device performance, for the slow growth procedure, is obtained at film thicknesses of approximately 300 nm, making it possible to optimize light absorption in these blends.

4.1 Introduction

Solar cells based on blends of conjugated polymers and methanofullerene derivatives continue to be of interest as promising candidates for low cost and large area photovoltaic devices. Up to now the 'state of the art' polymer solar cells are based on a combination of regioregular P3HT and [60]PCBM. For these cells it was demonstrated that a thermal annealing process of the complete devices resulted in an enhancement of the solar cell performance [1]. This enhancement of the power conversion efficiency (η) has been attributed to: an increase of the hole transport in the blend due to crystallization of P3HT, an improved film morphology, and a red shift of the absorption spectrum that results in a better overlap with the solar spectrum [2–4]. Li *et al.* have recently reported plastic solar cells based on a rr-P3HT:PCBM mixture with a power conversion efficiency up to 4%, which was realized by controlling the growth rate of the photoactive layer [5]. An efficient acceptor-type fullerene that can be used in solar cells based on rr-P3HT and other donor-type materials was synthesized in our group [6]. This fullerene derivative was designed to improve the compatibility with polythiophene donors by replacing the phenyl group of [60]PCBM with a thienyl one, resulting in [60]ThCBM. Previous results, shown in Chapter 3, indicate that [60]ThCBM gives the same charge carrier mobility as [60]PCBM and that a highly functional bulk heterojunction morphology can be readily obtained with rr-P3HT [6] as donor counterpart.

Previously it was demonstrated that high hole mobility can be obtained in field effect transistors with P3HT by using high boiling point solvents in the film casting process [7]. The microstructure of such devices was found to be highly crystalline, with a needle-like morphology. In the solar cell devices, high electron and hole mobility is desired to obtain good fill factors and high conversion efficiencies.

In this chapter, we study the influence of processing conditions by investigating the effect of the boiling point of the casting solvent on the morphology and transport properties of P3HT:[60]ThCBM photoactive layer. As is demonstrated in the following, this study provides insight in the relation between the microscopic morphology of the organic photoactive layer, the charge transport properties, and the performance of the bulk heterojunction solar cells. Additionally the thickness dependence of the solar cell performance was analyzed in detail.

4.2 Morphology

The morphology of the active layer film is a key parameter in understanding the device performance of the organic bulk heterojunction solar cells. The most common and practical tool to investigate the morphology of the organic films is AFM. Here AFM was used to investigate the morphology of the active layer of regioregular P3HT:[60]ThCBM blends that were grown at different rates by using solvents having different boiling points. Figure 4. 1 shows the AFM images of the P3HT:[60]ThCBM blend films cast from three solvents with different boiling points: chloroform (bp 61 ^{o}C), 2-methylthiophene (bp 113 ^{o}C), and ODCB (bp 173 ^{o}C). The films spin coated from chloroform solution were named fast growth active layers. Spin coating the photoactive layer from 2-methylthiophene and ODCB results in wet films, which were dried overnight at room temperature, in a closed Petri dish in nitrogen glove box. We refer to the layers obtained by the later method as slow growth active layers (more details can be found in Chapter 2).

The tapping mode AFM images of the fast grown films [see Figure 4. 1(a)] indicate that these films are less crystalline and have a granular surface topography without apparent whisker-like structures. The domain sizes are small, approximately 10 nm, and the domains consist of small crystalline P3HT chain like structures together with either pure [60]ThCBM or mixed P3HT:[60]ThCBM domains. Even though thermal annealing of the fast grown P3HT:methanofullerene films was found to enhance the P3HT crystallinity to some extent [4], the degree of crystallization remains limited by the time available for chain alignment, due to rapid evaporation of the solvent during the spin-coating process. Hence the interchain interactions, and consequently the device performance, are not optimal for fast grown films. For films spin cast from methylthiophene, however, one can see [Figure 4. 1(b)] that well-defined whisker-like structures with a width of approximately 15 nm and a length of more than 600 nm are formed during drying. Such well organized whisker-like structures are present over the whole surface and we attribute them, in agreement with literature, to crystalline P3HT domains [4, 8]. The vibronic structure of the absorbtion peaks (see Figure 4. 2) is much more pronounced for the slowly grown films, indicating a higher degree of ordering [9]. Compared with the fast grown film, the absorption shifts a little to the red in the slowly grown film. A red shift of approximately 37 meV appears in the better ordered films due to a better interchain π system overlap. It was previously shown that in a P3HT whisker morphology, the P3HT chains are lying normal to the long axis of the

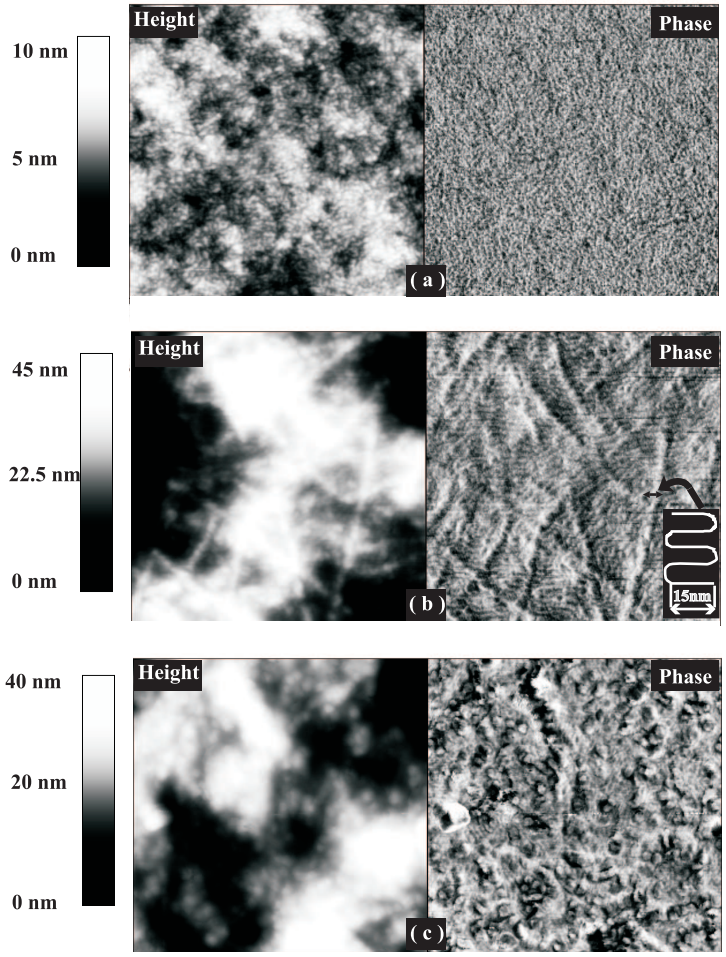

Figure 4.1: The $1 \times 1\mu m$ AFM height and simultaneously taken phase images of P3HT:[60]ThCBM blend films after the following treatment: fast grown spun from $CHCl_3$ (a), slow grown spun from methylthiophene, as inset the schematic representation for the whisker formation (b), and slow grown spun from ODCB (c). This pictures are taken for 200 nm active layer thickness of the fast grown film, and 300 nm active layer thickness of the slow grown films.

whisker and are folded with a period of approximately 15 nm [8, 10, 11]. This is in a good agreement with the topographical measurements shown in Figure 4. 1(b). Moreover, the films prepared from an ODCB solution have a different

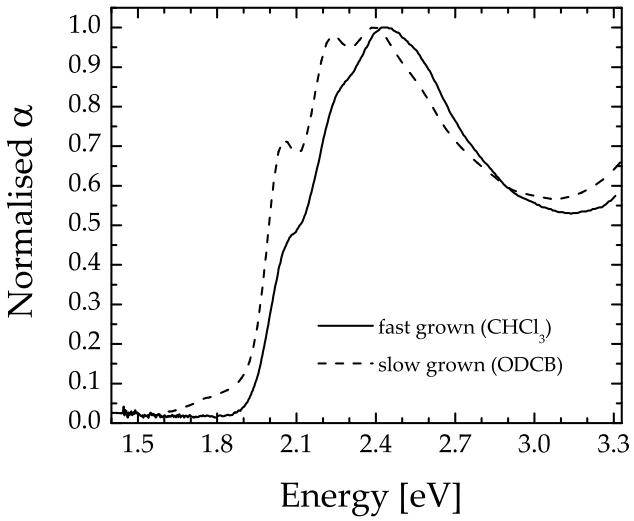

Figure 4.2: Normalized absorbtion coefficient (α) for fast and slow grown P3HT:[60]ThCBM blend films.

morphology compared to those prepared from methylthiophene, even though they were both grown under slow drying conditions. In case of films spun from ODCB, more pronounced [60]ThCBM crystallites are observed at the surface, and a phase separation into relatively large domains occurs. This indicates that the boiling point of the solvent is a critical factor in the polymer crystallization process as well as for finding the optimum film morphology in order to realize the best device performance [7]. ODCB has a higher boiling point (173 ^{o}C) than methylthiophene (113 ^{o}C). The drying time for films spin coated from ODCB solution is substantially longer under the same (atmospheric) conditions. It is known that [60]PCBM tends to crystallize in the pristine form and even crystallizes in blends with MDMO-PPV or P3HT [12, 13]. This is also the case for [60]ThCBM when blended with P3HT and spun from ODCB solution. The round shaped structures, which can be seen in the AFM image in Figure 4. 1(c), are between 20-30 nm in size and are presumed to represent the [60]ThCBM crystallites. The P3HT whiskers form a matrix, which is clearly visible in the phase images of Figures 4. 1(b) and 4. 1(c). The [60]ThCBM molecules diffuse out of the matrix and form large crystalline clusters for slow grown films from higher boiling point solvents (i.e., ODCB). Consequently, slower solvent evaporation facilitates the growth of highly crystalline films, which enhances polymer interchain interactions and thus improves the hole mobility significantly, as will be shown in the following section. However, this may have a negative effect

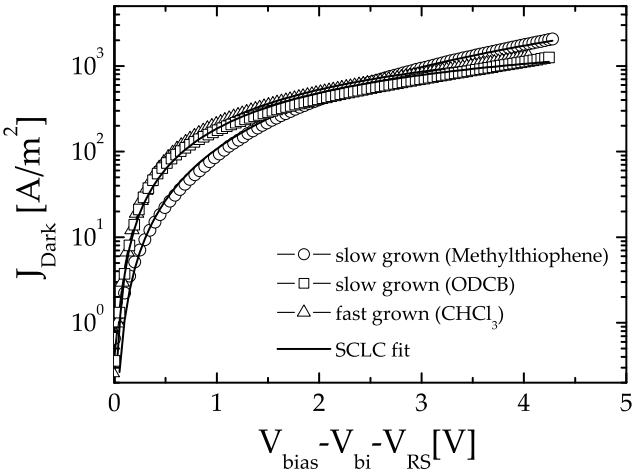

Figure 4.3: Experimental (symbols) and calculated (solid lines) J_{Dark}-V characteristics for ITO/PEDOT:PSS/P3HT:[60]ThCBM/Pd hole-only devices. J_{Dark} is plotted against the applied voltage (V_{bias}), corrected for the built-in voltage (V_{bi}) and the voltage drop over the ITO/PEDOT:PSS layers (V_{RS}). The thicknesses of the slow grown films are 270 nm, whereas the thickness of the fast grown film is 160 nm.

on the photocurrent of solar cells since phase separation into large domains will reduce charge generation as a result of the short exciton diffusion lengths, characteristic for conjugated polymers.

4.3 Hole transport

In organic bulk heterojunction solar cells charge carrier mobility in the active layer is determining the power conversion efficiency. Before discussing the solar cell performance of P3HT:[60]ThCBM blends, the charge carrier mobility in the blends, prepared with different growth rates, is evaluated. As shown in the previous section, slow drying of the P3HT:[60]ThCBM films using high boiling point solvents results in an enhanced crystallization of the P3HT phase, as compared with a fast drying procedure. Electron and hole mobility values are determined experimentally using various techniques including time-of-flight measurements [5], field-effect transistor measurements [7], and the analysis of the space-charge limited current (SCLC) [14] by investigating current density-voltage (J-V) characteristics in the dark. Figure 4. 3 shows the experimental dark current densities (J_{Dark}) of a hole-only device for fast growth as well as for slow growth of the active layer. The work function of PEDOT:PSS is 5.2 eV and therefore the PEDOT:PSS serves as an Ohmic contact for hole injection

into the HOMO of P3HT (4.9 eV [15]). On the other hand, the work function of palladium is 5.12 eV, which leads to a large mismatch with the LUMO level of [60]ThCBM [16], and it prevents injection of electrons into [60]ThCBM. When the applied voltage exceeds the built-in voltage (V_{bi}), J_{Dark} scales quadratically with the voltage V, indicative of space-charge limited (SCL) transport: $J_{Dark} \propto \epsilon_0\epsilon_r\mu V^2/L^3$,where $\epsilon_0\epsilon_r$ is permittivity of the polymer, μ charge carrier mobility, and L is the active layer thickness. For disordered semiconductors the electric field dependence of the μ must be considered: $\mu \propto \mu_0 \exp(\gamma\sqrt{\frac{V}{L}})$, where μ_0 is the zero-field mobility, γ is the field activation parameter which depends on the energetic and positional disorder of localized transport states. The combined equations provide for a direct determination of the charge carrier mobility [17–19]. The value of the hole mobility (μ_h), at zero electric field, was extracted by fitting the SCL dark current density (using the above equations) to the experimental data, as shown in Figure 4. 3. The hole mobility of P3HT in a blend with [60]ThCBM turned out to be the same for the films prepared by the slow growth method from methylthiophene and ODCB solution, and amounts to μ_h=2×10^{-3} cm^{2}V^{-1}s^{-1}. For the fast dried and thermally annealed P3HT:[60]ThCBM blend films, we determined a hole mobility of P3HT phase of 2×10^{-4} cm^{2}V^{-1}s^{-1}. Hence, applying slow drying, the hole mobility in the P3HT phase increases one order of magnitude with respect to the thermally annealed films. We conclude that during slow drying of the films, the P3HT has more time for reaching thermodynamic equilibrium, and the films have a high degree of ordering as can be seen from the absorption spectra, and therefore the charge transport in the P3HT phase is increased.This leads to a more balanced transport of electrons and holes in the device, since an electron mobility of ≈2×10^{-3} cm^{2}V^{-1}s^{-1} has been reported in P3HT:[60]PCBM blends for similar casting conditions [2, 20]. The fact that the hole mobility is identical in both slow grown films, despite of a difference in film morphology shown in Figures 4. 1(b) and 4. 1(c), is an indication that maximum crystallinity of P3HT is reached already at moderate growing times (moderate boiling point solvents). Most likely, further increasing the drying time of the blend films mainly results in the formation of more crystalline [60]ThCBM domains.

4.4 Solar cells characterization

After a study of the morphology and charge transport we proceeded with the analysis of the performance of the solar cell with photoactive P3HT:[60]ThCBM blend layers prepared under fast and slow growing conditions. All devices were

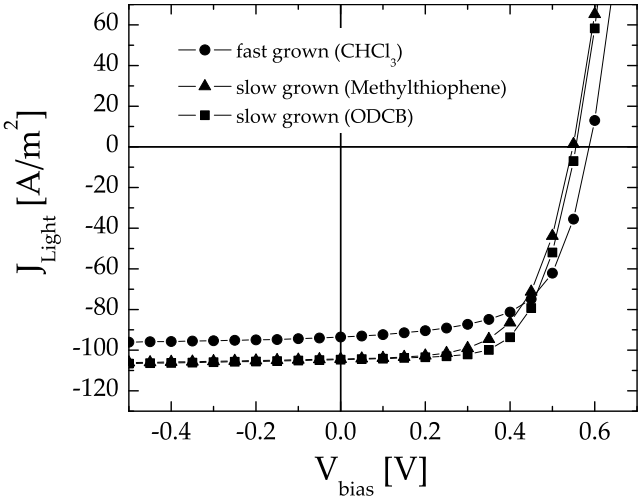

Figure 4.4: J_{Light}-V characteristics of ITO/PEDOT:PSS/P3HT:[60]ThCBM/Sm /Al devices with an active layer fast and slow grown. The slow grown films are 300 nm thick, and the fast grown film is 200 nm thick.

prepared as described in the experimental section. Figure 4. 4 shows the photocurrent (J_{Light}) of the solar cells in which the active layers were prepared by either fast drying and subsequent annealing, or by slow drying. The best device prepared by a fast drying procedure had a power conversion efficiency η = (3.1±0.2)%, a short-circuit current density Jsc = 90.8 A/m^2, an open-circuit voltage Voc = 0.59 V, and a fill factor FF = 59.3%. For the slowly dried films the best performance is obtained using an ODCB solution; with values of η = (3.5±0.3)%, Jsc = 99.5 A/m^2, Voc = 0.55 V and FF = 63%. The best device prepared from 2-methylthiophene showed a similar efficiency of η = (3.4±0.2)%. The better performance of the slowly grown devices, compared to the thermally annealed fast grown ones, most probably originates from an improved morphology and the subsequent enhancement of the hole mobility through the crystalline P3HT phase in the blend. In order to improve the device performance we also studied the influence of the thickness of the active layer on the solar cells performance. Figure 4. 5 shows the variation of the photovoltaic parameters as a function of active layer thickness. The devices fabricated by the slow drying method were all spun from ODCB. The Jsc is increasing rapidly with the active layer thicknesses for both slow and fast growth films until approximately 200-230 nm, indicating an efficient charge generation in these devices. At a P3HT:[60]ThCBM film thickness of 200-230 nm, most of the incoming photons are absorbed by the active layer. This is in agreement with previous results which showed that for

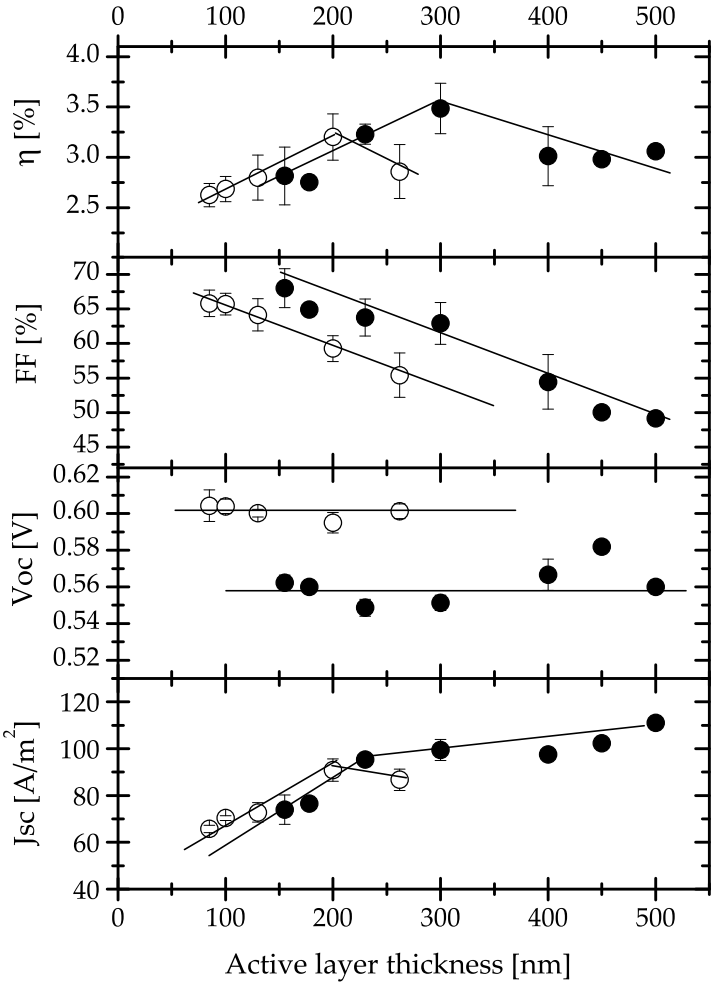

Figure 4.5: Device performance of the P3HT:[60]ThCBM blends, under illumination from a halogen lamp, as a function of the active layer thickness. The active layer was casted in two different ways: fast grown spun form $CHCl_3$ plus a subsequent thermal annealing step (empty circles), and slow grown spun from ODCB (full circles). The full lines are a guide to the eye.

a P3HT film of 240 nm more than 95% of the incoming photons are absorbed by the active layer within its spectral range [21]. Above 200 nm film thickness only a small fraction of photons from the solar spectrum remains to be absorbed and therefore the Jsc saturates. A small decrease in Jsc for fast drying films for thicknesses above 200 nm can be attributed to the limitation imposed on Jsc by space-charge effects and/or charge recombination. These effects are a con-

sequence of an unbalanced electron and hole transport which is present in the blend and is caused by a lower hole mobility of P3HT phase [22, 23]. The Voc is relatively constant as a function of active layer thickness, with a larger voltage produced by the fast dried and annealed devices. This difference in voltage of approximately 40 mV is fully accounted by the red shift in absorbtion spectra (37 meV) as a result of the enhanced crystallinity of P3HT in the slow grown films (see Figure 4. 2). The reduction of the optical gap of P3HT is a consequence of the decrease in ionization potential (HOMO level) by an enhancement of the intermolecular overlap. It appears to be in agreement with a simple model calculations which confirm the reduction of the band gap and find that about $\frac{3}{4}$ of the shift occurs in the valence band [24]. Since the Voc of donor:acceptor bulk heterojunction solar cells is linearly related to the $HOMO_{donor}$-$LUMO_{acceptor}$ energy difference [16], the Voc is lowered when the ionization potential of the donor is decreased. Consequently the Voc is lowered in slow grown films. The FF is decreasing linearly with the layer thicknesses for both, fast and slow growth methods, due to increasing recombination of charge carriers by increase of the mean distance they need to travel before they are extracted at the electrodes. Moreover the FF for the slow growth films is in average 10% higher for the same film thickness, compared to the fast growth films, as a result of a better and more balanced transport of electrons and holes in the device (see previous section). Consequently, the difference in conversion efficiency between slow and fast growing films is mainly determined by the difference in FF and Voc for the same film thickness. Although the Voc is lower for slow growth films its superior fill factors well compensate the loss in Voc and therefore result in a better overall cell performance. The benefit of an improved charge carrier mobility for slow growing films together with a better balanced electron and hole transport makes it possible to manufacture thicker active layers without significant loss in FF, and therefore it allows to maximize charge generation in these blends.

4.5 Conclusion

In conclusion, we have shown that slow growing of the active layer films in P3HT:[60]ThCBM blends, by using solvents with a high boiling point, facilitates growing of highly crystalline films. This enhances the interchain interactions in the P3HT phase, and improves the hole transport in the blend by an order of magnitude. This leads to a well balanced charge carrier transport in the blend. The difference in power conversion efficiency between slow and fast grown films is mainly determined by the difference in the fill factor and open-

circuit voltage of the cells. Although the open circuit voltage tends to be lowered (with approximately 40 mV) in devices with active layers with a higher degree of molecular organization, it is the significant increase in the fill factor (up to 70%) which gives much higher (13% relative) power conversion efficiencies. The benefit of better charge transport for slow growing films makes it possible to fabricate thicker films without significant loss in fill factor, and therefore it allows for maximizing light absorption in these blends.

In the next Chapter a study of the lifetime of the bulk heterojunction photovoltaic devices, with a slow growth P3HT:methanofullerene photoactive layer, will be presented.

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